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13. ABSTRACT *(Maximum 200 words)*

A combination of electron beam lithography, reactive ion etching and low temperature vapor deposition was employed to produce ultra-small one- and two-dimensional arrays of tunneling junctions, and wires of small cross sectional area. The original goal, the production of side-by-side junctions, with tunneling occurring between metal electrodes in a plane rather than through an insulator could not be realized. Transport properties of wires with extrememly small cross-sectional areas were studied.

Tunneling junctions with solid inert gas barriers and metallic electrodes were prepared. The motivation for this work was to produce junctions on high temperature superconductors with robust barriers whose processing did not involve chemical reactions at the interface. Our approach was successful, although tunneling resistances have thus far been too high to observe the energy gap in a superconducting electrode.

Heterostructures of cuprate superconductors and manganite ferromagnets were grown by MBE. The suppression of critical currents and critical temperatures by spin injection wass observed, and the interfacial resistance across the boundary between the ferromagnet and the superconductor investigated. The effects observed are believed to be a consequence of the high degree of spin polarization in half-metallic manganite films, and may be the basis for a new superconducting device technology.

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FINAL REPORT

"Tunneling and Transport in Mesoscopic Structures"

OFFICE OF NAVAL RESEARCH

Grant #N00014-92-J-1368

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1 March 1992 through 28 February 1998

June 1998

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1.0 Summary

This program has involved two tasks. In the first, superconducting and normal state properties of arrays of ultrasmall tunneling junctions and ultrathin wires were investigated. A combination of electron beam lithography, reactive ion etching and low temperature vapor deposition was employed in an attempt to produce ordered and disordered one- and two-dimensional arrays of junctions with small capacitances, and wires of small cross sectional areas. It was found not practical to make side-by-side junctions, with tunneling occurring between metal electrodes in a plane rather than through an insulating layer. Wires with small cross-sectional areas were formed successfully, and their transport properties were studied at low temperatures.

The second task involved two projects. The first was the development of planar structures in which single crystal films of high-T_c superconductors (HTSC's) were overlaid with metallic and insulating films. The goal was to process the structures using *in situ* techniques so as to avoid interfacial chemical reactions and interdiffusion between layers which are unavoidable in all commonly used methods of forming planar junctions. Tunneling junctions with solid inert gas barriers were developed. Structures with metallic electrodes were produced with insulating barriers, but tunneling resistances have thus far been too high to observe either the superconducting energy gap, or excitations in the superconducting electrode.

As part of the second task we grew, using molecular beam epitaxy (MBE), heterostructures of cuprate superconductors and manganite ferromagnets. In this work we observed suppression of critical currents and critical temperatures by spin injection, and investigated the interfacial resistance across the boundary between the ferromagnet and the superconductor. The effects observed are believed to be a consequence of the high degree of spin polarization in half-metallic manganite films which also exhibit the phenomenon of colossal magnetoresistance. These phenomena may serve as the basis for a new superconducting device technology.

2.0 Technical Accomplishments

2.1 Task 1: Tunneling and Transport in Mesoscopic Structures

2.1.1 Introduction

Arrays of ultra-small junctions are model systems for mesoscopic superconducting phenomena, and wires which are sufficiently small in cross sectional area exhibit 1D transport. The properties of such systems are an important part of the science base for single-electron-tunneling devices, and array configurations can be used directly as generators of radiation or sensors.

This task was focused on the development of innovative techniques for the fabrication of ultra-small tunneling junctions and junction arrays, and ultrathin wires, i.e., mesoscopic structures. Some years ago its scope was diminished relative to the work on heterostructures, described in Task 2. The goal was to fabricate mesoscopic structures using a combination of electron beam lithography, reactive ion etching and low temperature vapor deposition. The original plan was to fabricate junctions of a unique side-by-side type, with the tunneling between metal electrodes in the plane rather than through an insulating layer separating two planes. This approach could be called the shadow evaporation technique. Wires would be formed by angled evaporation into a corner of a channel cut in a substrate, with the wire width constrained by the shadow of the far wall of the channel. Our work demonstrated that single insulating junctions and linear arrays of insulating junctions could be produced using the proposed shadow-evaporation technique, but in 2D only weak link arrays or extremely disordered junction arrays were feasible. However, this approach was found to be useful for producing wires of extremely small cross-sectional area. The cross-sectional dimensions of the wires could be further reduced by angled reactive ion etching. In the end, the structures studied at low temperatures were produced using more conventional approaches which were more convenient to implement.

2.1.2 Accomplishments

2.1.2.1 Shadow Evaporated Structures

We used the Cornell Nanofabrication Facility to develop the nanometer-scale lithography required to fabricate the small structures needed for the preparation of junctions, junction arrays, and ultra-small wires by the shadow evaporation technique. We grew a number of bow-tie-shaped tunneling junction structures. We found that these junctions can be accurately modeled as sharp scanning tunneling microscope tips. A typical radius of curvature for an STM tip is roughly 2000 Å; approximately five times larger than the base of the bow tie which defines a junction. A bow tie junction's resistance has been found to be at least as sensitive to tunneling distance as an STM tip, leading to a severe requirement on junction uniformity to achieve a 2D insulating junction array. This in turn sets a requirement of extraordinarily accurate positioning of the contact mask array structure relative to the incoming evaporant beam to prevent the system from becoming strongly anisotropic. This uniformity requirement makes it very difficult to prepare an array of insulating junctions with uniform coupling. Since individual atoms are typically several angstroms in diameter, each island would have to be identical to within a few atoms. Because even the most precise e-beam lithography techniques are not able to control line widths to within one atom, arrays with insulating junctions, produced using this technique would probably be extremely disordered. Thus we concluded that we should not pursue the fabrication of insulating 2D arrays. However, an account of this approach to fabrication of structures was published in Applied Physics Letters[1].

To carry out the shadow depositions described above, a deposition system with precise angular alignment of liquid helium cooled substrates with respect to the direction of deposition, and *in situ* ion etching capability which can also be used with liquid helium cooled substrates was assembled. This fabrication system is equipped with three Knudsen cells which are able to reach temperatures as high as 1400°C. It is also equipped with a RF ion source which can be used with variety of gasses (H_2, He, Ar, Xe, N_2, O_2). Most importantly, the samples are mounted on a cryostat capable of reaching a base temperature of 1.6 K. Therefore, measurements can be performed without having to break vacuum. Because the cryostat is coupled to the vacuum chamber through a rotatable flange, the etching angle and hence the cross-sectional area can be changed continuously. This equipment, intended for use in fabricating shadow-evaporated junction structures, because of its etching and deposition capabilities, became central to Task 2 and to the follow-on ONR Grant in which precision lithography is required for the development of spin-injection devices.

2.1.2.2 One Dimensional Superconducting Wires

The structures which were ultimately studied at low temperatures were fabricated using a conventional combination of electron beam lithography, reactive ion etching and vapor deposition. The focus was on studying superconducting wires which were sufficiently small in cross sectional area to exhibit 1D transport. As mentioned above, the properties of ultra-small junctions and wires are part of the science base for single-electron-tunneling devices, and also must be understood to engineer Josephson junction array configurations which can be used as generators or sensors of electromagnetic radiation.

The primary goal of studies of transport properties of ultra-small cross sectional area superconducting wires is to determine whether their resistance at low temperatures is a consequence of macroscopic quantum tunneling of phase slip centers, or follows from Coulomb effects encountered in the transition to 1D behavior, the two explanations which have been suggested. We studied the smallest wires we could make, and carried out measurements at very low temperatures in an electromagnetically shielded environment. As there is currently no rigorous theory of the of any of the phenomena, our approach has been to characterize in a comprehensive way a number of properties which can then be used to test a future theory.

The electrical transport properties of narrow superconducting wires were studied as a function of temperature and magnetic field. The wires used were two orders of magnitude smaller than samples studied extensively in the 1970's and modeled successfully using phase slip center (PSC) theory. The PSC theory assumes that dissipation in 1D superconducting systems occurs from spatially localized regions of the superconductor which oscillate between superconducting and normal states.

Recent results have indicated that the electrical transport behavior of our samples cannot be explained even qualitatively within the context of PSC theory. Within 50 mK of T_c, I-V curves from these wires show a striking negative differential resistance in zero field which can not be explained within PSC theory. The application of a small magnetic field applied parallel to the direction of current eliminates this feature but otherwise leaves all other structure in the I-V curves unchanged. Approximately 150 mK away from $T_c(H=0)$ and within 200 Oe of H_c, we find that the resistance (i.e. V/I) over a certain range of current is larger than the normal state resistance. Again, this result cannot be explained using PSC theory. At low temperatures, we find different but still unexpected behavior. At fields close to H_c, a staircase structure appears in the I-V curves, similar to what had been seen in larger samples in the 1970's. These steps however do not appear to be caused by phase slip centers. Quantitative estimates from the steps cannot be reconciled with fundamental predictions of PSC theory.

Our data described above indicate that these narrow wires are governed by physics very different then what governs their older, wider predecessors. At the present time there is no physical model. We plan to publish a brief account of this work in the Brief Reports section of Physical Review B to in essence test the waters of the theoretical community. Also an account of the wire fabrication technique is of technological interest and will be published in an appropriate techniques journal such as Review of Scientific Instruments.

2.2 Task 2: Interface Structures and Tunneling Junctions

2.2.1 Introduction

This task has had two foci. One has been the development of tunneling structures with high-T_c superconducting films for the elucidation of the physics of superconductivity.

Our unique approach has been to process the structures using *in situ* techniques which avoid interfacial chemical reactions and interdiffusion between layers which are unavoidable in all of the usual junction fabrication techniques. This has involved using an inert gas buffer layer of Xe as the barrier so as to avoid chemical effects at the superconductor surface. The metallic counterelectrode is then deposited on top of the Xe layer. Junctions prepared in this way can provide baseline information on tunneling characteristics for comparison with those obtained with more conventionally prepared junctions. Although the ultimate goal of the work was not realized, remarkable progress was made, and the approach appears feasible.

In parallel with the above was an effort to develop interfaces between oxide superconductors and other oxide materials. This work has evolved into a new ONR grant. We have produced very high quality high-T_c and doped lanthanum manganite films possessing smooth ordered surfaces using the technique of ozone-assisted molecular beam epitaxy MBE in the block-by block mode[2,3,4]. We have succeeded in juxtaposing films of compounds such as $DyBa_2Cu_3O_{7-x}$ and $La_{1-x}Sr_xCuO_4$ to produce single crystal heterostructures[6]. These may be the basis of a new class of devices based on nonequilibrium effects associated with spin injection into superconductors.

2.2.2 Accomplishments

2.2.2.1 Junctions with Inert Gas Barriers (co-funded by NSF)

The initial goals of this work were not achieved at the completion of the grant. However the research is being continued using institutional resources, as the desired junctions appear realizable. Future publications will acknowledge the support of this particular ONR grant. Since we have not published anything relating to this work, we will describe our accomplishments below.

To avoid the complexities of high temperature superconductors, we began by attempting to grow Pt/Xe/Pb tunneling junctions. The base layer was Pt, which could be deposited as a very smooth layer, and the counter electrode was quench-evaporated Pb.

The idea behind using this combination was that the observation of the energy gap in Pb, and the phonon spectrum of Pb would be strong tests of tunneling. These features would then establish proof-of-principle.

Four-probe electrical measurements were made on the Pb/Xe/Pt junction and the Pb strip. The Pt strip was measured using a two-probe technique. Care was taken to keep the temperature below the transition temperature of the Pb and to run low currents so that the Xe layer was not heated significantly and changed.

At low voltages, the current was a linear function of voltage with a resistance of 920 MΩ. At higher voltages there is a term which is cubic in voltage. This is shown in Fig. 1. Unfortunately we have as yet no evidence of the superconducting gap or the phonon spectrum of Pb. Further work should change this. These first successes produced very high resistance junctions. A one mV change in voltage corresponds to one pA of current which is just at the limit of the resolution of our apparatus. We are nevertheless quite optimistic.

First the I-V characteristic of Fig. 1 is unique to the junction. We show R(T) for the Pb film measured at low current in Fig. 2. The superconducting transition temperature is about 7K. This is on a film which has been gown on top of a solid Xe barrier! The Pt film, on the other hand, has a linear I-V characteristic up to currents much higher than those at which the junction exhibits a cubic term, which strongly suggest that the I-V curves of Figs. 1 are due to tunneling through the Xe layer.

Attempts were made to lower the resistance of the junction to obtain data with less noise. This was only partially successful. Successive cycles of heating to 25K resulted in ultimately reducing the junction resistance to 7.8MΩ, but no Pb gap or Pb phonons were observed. The heating technique when repeated further usually resulted in the Pb and Pt layers being shorted.

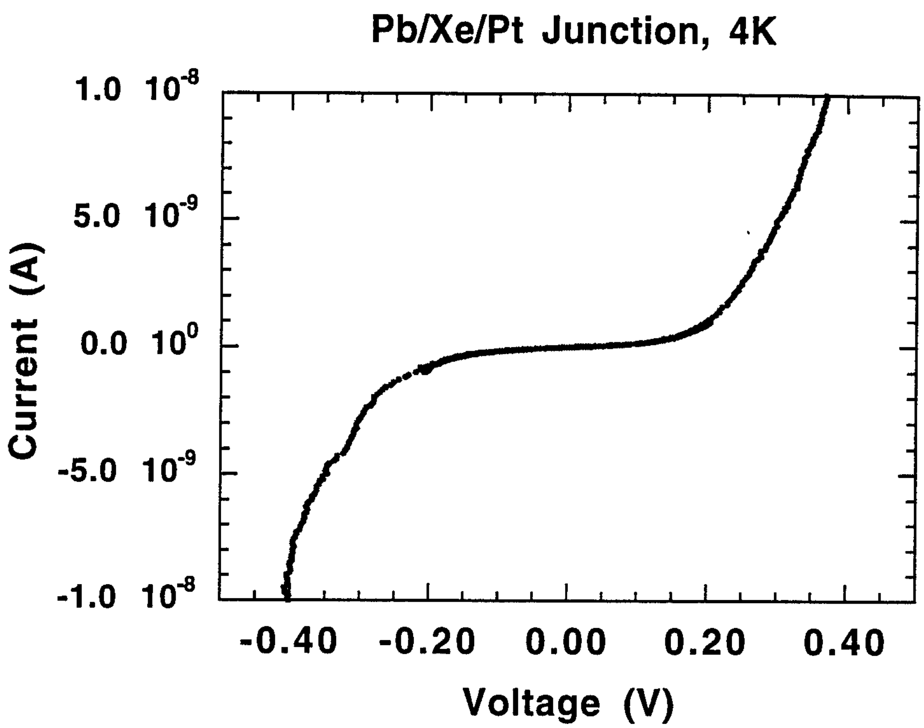

Fig. 1. I-V characteristic of the junction.

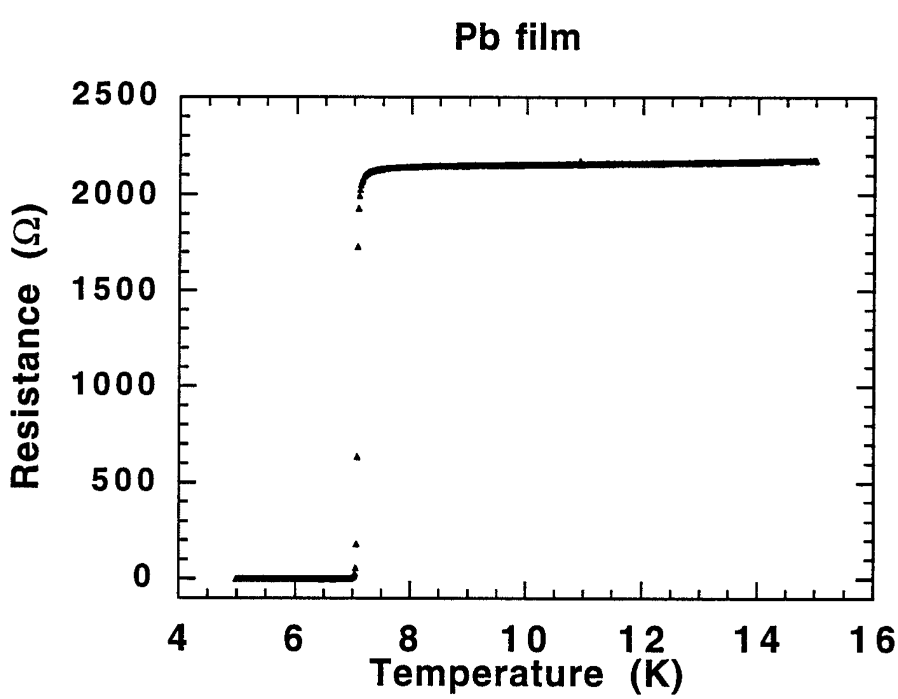

Fig. 2. R(T) of the Pb film showing a superconducting transition near 7K.

It is clear that it will be necessary to control the junction resistance at the outset, by reducing the amount of Xe deposited. This step is currently under way. There is of course no guarantee of success as the Xe layer will need to be thinner than the 100Å thickness in which has been achieved thus far.

We are currently continuing this work using other funds, and if we are ultimately successful we will publish the results. This approach to tunneling barrier fabrication may have other impacts on the use of tunneling in systems other than high temperature superconductors. It may provide an alternate route to fabricate junctions used to study chemical compounds using inelastic electron tunneling spectroscopy.

2.2.2.2 Manganite/cuprate Interface Structures

The most exciting results were associated with the development of techniques for juxtaposing superconducting cuprate films with films of rare earth doped manganites such as lanthanum strontium manganite. The latter materials exhibit large negative magnetoresistance. Because manganite compounds are half-metallic, their charge carriers are spin-polarized.

We have found that the critical currents of thin films of high temperature superconductors are strongly suppressed when carriers from a manganite film are injected into them[6]. As a consequence of control experiments, we believe that this observation results from the injection of spin-polarized carriers. *In situ* studies of reflection high energy electron diffraction have revealed that cuprate and manganite layers form in a compatible way. Ordered crystal structures form at the boundary. Other structural and chemical studies support the view that the boundary between the two films is highly ordered. These spin injection experiments have been the subject of numerous invited talks, including the 1998 APS March Meeting, the Santa Barbara conference on Quantum Systems Far from Equilibrium in the summer of 1997. Additional talks will be presented at the workshop on manganites to be held during the summer of 1998 in Telluride Colorado, the SPIE meeting in San Diego, the manganite workshop at Michigan State University in

East Lansing, the American Vacuum Society meeting in Baltimore in the Fall of 1998, and at both the Fall 98 and Spring 99 Materials Research Society meetings.

There are also additional results on magnetic/superconductor interfaces[7]. Investigations of the I-V characteristics of boundaries indicate that Andreev transport through the boundaries may be severely inhibited with spin-polarized carriers. We have observed a dip at zero bias in the conductivity at such boundaries. Its half width of about 30 to 40mV is of the order of the amplitude of the superconducting gap in a 90K high temperature superconductor, and depending upon the sample, the effect vanishes at either 60K or 90K. It is not particularly magnetic field sensitive up to fields of the order of 12T.

We have hypothesized that we are observing a consequence of the half metallic nature of the magnetic half of the bilayer structures in which the effect has been seen. For metal/superconductor sandwiches, with no barrier separating the metal and superconductor, one would expect subgap conductance to be greater than the normal conductance at injection energies in excess of the gap. This is because of Andreev reflection. An electron incident on the superconductor from the metal is not an allowed excitation in the superconductor if its energy is less than the gap. It is consequently retro-reflected as a hole, and a Cooper pair propagates into the superconductor. The combined electron and retro-reflected hole result in a current twice that of the ordinary normal conductance which would result if the electron were an allowed excitation in the superconductor.

If the metal is a half-metallic ferromagnet, then the retro-reflected hole, because it must have its spin flipped is not an allowed excitation, and the process is suppressed. Thus for an *s*-wave superconductor, in the absence of any boundary scattering one might expect to see the conductance below the gap vanish. If the superconductor is anisotropic, there will be a directional averaging over the values of the gap. The feature we have observed is qualitatively consistent with such a picture.

3.0 Personnel

Allen M. Goldman	Professor
Vladislav Vas'ko	Research Assistant (Ph.D to be granted, Fall 1998)
Catherine Christiansen	Research Assistant (Ph.D expected, Spring 2000)
Konstantine Nikolaev	Research Assistant (Ph.D expected, Fall 2000)
Eric Olson	Research Assistant (Left 1996)
William Huber	Graduate Dissertation Fellow and Research Assistant (Ph.D expected, December 1998)

4.0 Publications Supported by the Grant

1. "A New Method for Fabricating Ultra-narrow Metallic Wires," E. Olson, G.C. Spalding, A.M. Goldman, and M. J. Rooks, Appl. Phys. Lett. **64**, 27740 (1995).
2. "Growth of La-Ca-Mn-O films by ozone-assisted molecular beam epitaxy," by V. S. Achutharaman, P. Kraus, V.Vas'ko, C. Nordman, and A.M. Goldman, Appl. Phys. Lett.**67**, 1019 (1995).
3. "Ultrasmooth, highly ordered, thin films of $La_{0.67}Ca_{0.33}MnO_{3\pm d}$" V. A. Vas'ko, C. A. Nordman, P. A. Kraus, V. S. Achutharaman, A. R. Ruosi, and A. M. Goldman, Appl. Phys. Lett. **68**, 2571 (1996)
4. "Magnetic and electrical properties of the ferrimagnet $Dy_{0.67}Ca_{0.30}MnO_{3\pm d}$," C. A. Nordman, V. S. Achutharaman, V. A. Vas'ko, P. A. Kraus, A. R. Ruosi, A. M. Kadin, and A. M. Goldman, Phys. Rev. B **54**, 9023 (1996)
5. "Magnetoresistance in Layered Manganite Compounds," A. M. Goldman, Science **274**, 1630 (1996).
6. "Critical Current Suppression in a Superconductor by Injection of Spin-Polarized Carriers from a Ferromagnet," V. A. Vas'ko, V. A. Larkin, P. A. Kraus, K. R. Nikolaev, D. E. Grupp, C. A. Nordman, and A. M. Goldman, Phys. Rev. Lett. **78**, 1134 (1997).

7. "Differential conductance of the ferromagnet/supercondctor interface of $DyBa_2Cu_3O_7/La_{2/3}Ba_{1/3}MnO_3$ heterostructures, V. A. Vas'ko, K. R. Nikolaev, Va. A. Larkin, P. A. Kraus, and A. M. Goldman, accepted for publication in Appl. Phys. Lett.

8. "Selective epitaxy of $DyBa_2Cu_3O_7$ using an amorphous $Dy_{1-\delta}Cu_{\delta}O_x$ template," P. A. Kraus, W. H. Huber, and A. M. Goldman, accepted for publication in the Journal of Materials Research.

5.0 Invited Talks

1. Rice University Physics Colloquium, October 1996
2. Argonne National Laboratory Materials Science Colloquium, January 1997
3. SUNY Stony Brook, Condensed Matter Physics Seminar, February 1997
4. QUEST Workshop on Quantum Systems far from Equilibrium, University of California at Santa Barbara, August 1997.
5. Workshop on Magnetism and Superconductivity, California Institute of Technology, March 1998
6. American Physical Society March Meeting, Los Angeles, California, March 1998